CHAPTER XXVII PRODUCTION OF MAGNESTUP, BY ELECTROLYSIS OF ITS OXIDE AND OF MODRESION ALLOYS WITH OTHER METALS STAT	 Declassified in Part - Sanitized Copy Approved for Release 2012/05/10 : CIA-RDP82-00039R000100230042-0		0747
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Chapter XXXII

PRODUCTION OF MAGNESIUM BY ELECTROLYSIS OF ITS OXIDE
AND OF MAGNESIUM ALLOYS WITH OTHER METALS

103 - Production of Magnesium by Electrolysis of Magnesium Oxide.

Production of Magnesium by electrolysis of its oxide (the so-called Oxide method) has been studied by a number of researchers. Reason for interest in this method is a desire to avoid the very complex and costly process of obtaining anhydrous chloride salts for their subsequent electrolysis.

Success in producing aluminum by the electrolysis of alumina (aluminium oxide) in fused fluorine salts, naturally led to the idea of applying an analogous process to magnesium oxide.

However, during the development of the process of direct electrolysis of magnesium oxide in fused agents, certain difficulties were encountered which have, as yet, not been solved for industrial application.

The basic difficulties usually connected with this process are:

(1) the very low solubility of magnesium oxide (tenths of a percent)
in compounds suitable as smelting agents for the electrolytic production
of pure magnesium; this results in frequent anodic complications that
interrupt the process of electrolysis; (2) high melting temperatures of
these agents (950 - 1000 degrees /centigrade/) resulting in considerable
loss of magnesium during the electrolysis process (evaporation, reoxidation);
(3) high (as compared with metalic magnesium) specific gravity of the
molten electrolyte, thus complicating the creating of an efficient electrolyser so as to prevent considerable loss of the separated metal.

Should these shortcomings be eliminated, the oxide method, on account of its simplicity, may present advantages as compared with existing methods of producing magnesium by the electrolysis of fused chlorides.

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Should these shortcomings be eliminated, the oxide method, on account of its simplicity, may present advantages as compared with existing methods of producing magnesium by the electrolysis of fused chlorides.

In the production of Magnesium by electrolysis of Magnesium Oxide, a fused compound of ${\rm MgF}_2$, NaF, KF and ${\rm BaF}_2$ is usually used as a solvent.

Theoretical voltage of decomposition of MgO in such an electrolyte at 950 degrees /centigrade/ is 2.45 volts with a platinum anode and 1.34 volts with a carbon anode. (M. Thomson, Trans. of the Elektroch. Soc, 1935,165).

The first important plant to produce Magnesium by electrolysis of Magnesium Oxide in fused fluorides was installed by the American Magnesium Company at Niagara Falls(Harvey, Chem. metal Eng., 32,573,1925). Production was, however, suspended after a year's operation.

The electrolyser (figure 198, Harvey Electrolyzer) used in this case consists of an iron shell devoid of any heat insulation or lining.

The latter is formed by solidification of the electrolyte on the bottom and side walls in layers 15-25 centimeters thick, serving simultaneously as heat and electric insulation. The iron cathodes pass underneath through the shell of the bath. Two rows of carbon anodes immersed in the electrolyte are suspended overhead. The anode and cathode areas are separated by two diaphragms, formed by a layer of solidified electrolyte on pipes cooled by water. As an electrolyte, a melt of equal parts of MgF2 and BaF2 with an addition of a suitable quantity of NaF to melt approximately 950 degrees, is used. The presence of BaF2 increases the density of the molten electrolyte up to 3.2 /grams per cubic centimeter/ and facilitates the rise of the segregated magnesium to the surface of the electrolyte. The metal collects on the surface under the crust of the frozen electrolyte above the cathodes and is periodically ladled from the bath.

Magnesium oxide is added to the electrolyte near the anodes.

Since the solubility of MgO in such an electrolyte is only O.1 percent it appears that MgF_2 is first subject to electrolysis, while the separating fluoride reacts with magnesium oxide suspended in the electrolyte.

The electrolysers described worked at 9000/13000 amperes and 9-10 volts.

In view of the high temperature of the electrolyte and frequent anodal effects, electric current efficiency did not exceed 50 percent, while energy efficiency was only 10 percent. The metal produced contained 99 percent Magnesium with iron, silicon, aluminum and traces of barium as impurities. Subsequent resmelting produced metal of 99.9 percent purity. Thanks to the non-hygroscopicity of the electrolyte, magnesium thus produced is very corrosion resistant.

Considerable research on the subject of producing magnesium by electrolysis of MgO dissolved in fused fluoride salts, was conducted by Grube and his associates (1927-1930). (Z. F. Elektroch. 1927, XXXIII, 48; ibid 1930, XXXIV.) These researchers studied the ternary fusion diagrams

Determining the solubility of MgO in these systems revealed that the solubility of MgO is determined, primarily by the presence of NaF in the melt; the more NaF the higher the solubility of magnesium oxide.

Table 81 shows the results of Grube's experiments in the electrolysis of MgO in melts of different compositions.

RESULTS OF EXPERIMENTS IN THE ELECTROLYSIS

OF MgO IN FLUORIDES

(BY GRUBE)

No. of Melt	Composition of electrolyte, %			Temperature	Current	
	MgF ₂	BaF2	NaF	during process	yield in % of Mg	
1 2 3 4	18 21 35 40	50 71 256 40	32 8 8 11	800 850 900 950	4 25 50 40	

From table 81 it follows that electrolyte No 1, in spite of the low fusion temperature (750 degrees) and comparatively high solubility of MgO (about 1 percent), practically produces nothing but sodium. The

The electrolysis of melt No 2 with a fusion temperature of 800 degrees resulted in a 25 percent electric current yield of Magnesium due to the simultaneous segregation on the cathode, of magnesium and sodium, the latter by raining on the surface. On the contrary melt No 3, in spite of its low solubility of MgO (0.25 percent) segregates primarily metallic magnesium (current yield 50 percent).

The reason for this phenomenon is that in the combination NaF-MgF2 (figure 199)(Fusion Diagram for the System NaF, MgF2); this fusion has great importance in the possibility of segregating magnesium from fused fluoride salts at acceptable and practical current yields.

If free sodium fluoride is present in a given concentration of components in a melt in accordance with the fusion diagram, primary separation will be metallic sodium. If, however, sodium fluoride, contained in the melt, is combined with magnesium fluoride in the form of MgF₂, NaF and, in addition there is a further abundance of Magnesium fluoride, then the cathode product is pure Magnesium.

However, the drawback in this case is the low solubility of MgO in melts, resulting in frequent disruption of the process through anodio effects.

The French researcher F. Ran... (1931-1932)(Chemie et Ind. No 6, 1931, V. 26, 1261-1270; ibia, January 1932, V. 27, 31-40) published results of his experiments on the electrolysis of MgO, based on data of prior researchers. He analyzed electrolytes composed of various combinations of MgF₂, CaF₂, BaF₂ and NaF with small additions of MgO. Ran... confirmed by his own experiments conclusions of earlier researchers that when the electrolyte contains a considerable quantity of NaF the main product of electrolysis is Sodium.

To combat anodic effects, Ran... recommends a lowered anodic current density (below 20 amperes per square inch) and use of anodes with the least possible porosity.

Several Institutes in the USSR (Gin vetmet, Mingvetmetzoloto, MosVAMI) have repeatedly experimented with the process of producing Magnesium by electrolysis of MgO in fused fluorides.

These experiments have confirmed, that in principle, it is possible to obtain magnesium by this method. At the same time they also demonstrated that for a practical application of this method further research is necessary to find melts with a lower melting temperature, a larger solubility vis a vis MgO and with a relatively small content of NaF. Experiments of MosVAMI, showed, among other things, that an addition of KF to the electrolyte is quite beneficial.

Thus, according to A. I. Hazanow, (Soviet Authors' Certificate

No 47447 dated 30 June 19??) an electrolyte composed of three molecules

MgF2 and diverse molecular quantities of KF, NaF and BaF2, fuses at a

temperature of approximately 900 degrees and is the most acceptable for

the electrolysis of MgO. Up to 3 percent MgO dissolves in this electrolyte.

Current yield of Magnesium during the electrolysis process attained

80 percent at a 940 degree working temperature of the electrolyte.

This process may be accomplished in an electrolyser, lined with magnesite,

characterized by high stability and absence of anodic effects due to

considerable solubility of MgO in the electrolyte.

104 - Production of Magnesium Alloys by Electrolysis.

Under existing methods of obtaining metallic Magnesium, the latter being lighter than the molten electrolyte, rises to the surface. This fact complicates the construction of a bath, requiring separate anode and cathode areas and is also a reason for the loss of metal due to oxidation on contact with air.

Numerous suggestions have been made on how to isolate the magnesium on a molten metallic cathode, heavier than magnesium, such as aluminum, lead, zinc, copper and others. In that case it would be possible to conduct the electrolysis process in an electrolyser of a standard type, without a diaphragm, and obtain a magnesium alloy heavier than the electrolyte, on the surface of the lower total.

A melt thus produced may be used directly as an

alloy in the production of magnesium alloys or the magnesium may be extracted by one method or another (for example by volatization) in very pure form.

Unfortunately up to this time, these suggestions have not received any industrial acceptance. The main reason for this is the formation of sludge in the bath. The sludge settles on top of the liquid metallic cathode, considerably increases its electrical resistance and thus disrupts the process.

Nevertheless a number of experiments undertaken along this line, at times on a large scale, prove that in principle this process is feasible.

Let us describe a few of the more interesting ones:-

Systematic research for direct production of magnesium alloys by electrolysis was originally conducted by R. Weiner (Z. F. Elektroch, 38, 232, 1932), who managed to electrolyze fused magnesium chloride on a liquid aluminum cathode. The process was performed at 50-120 amperes. Temperature 600/650 degrees and density of current 1.5 amperes per square centimeter.

Saturation of the melt with Magnesium without its rising to the surface was possible up to 90/91 percent Magnesium. Power consumption was 13-15 kilowatt hours per 1 kilogram magnesium.

Japanese researchers I. Namari and T. Ishiko (The Journ. of the Chem. Ind. Japan No 10, 1935) experimenting on a small scale (at approximately 30 amperes) showed that the best electrolyte for this process is magnesium chloride with a small addition (5-10 percent) of NaCL; this permits the process to be conducted at a temperature of approximately 670 degrees with an average current yield of 94 percent. Alloys obtained by these researchers contained approximately 50 percent aluminum and 50 percent magnesium.

Here in USSR, B. Popo (Report VAMI, No 461, 1935) conducted research on the production of magnesium-aluminum alloys by electrolysis of carnallite on liquid aluminum cathodes. He conducted the electrolysis in an electrolyser at 300 amperes, a current density of 1.5-2 amperes per square centimeter and a temperature of 660 degrees.

Finally V. Gustkov and H. Stradet (Metallurgist, No 10, 1936) studied the process by electrolysis of magnesium and zinc alloys. Carnallite was used as the electrolyser and at optimum conditions were found as follows: Temperature within a range of 660-680 degrees and cathode current density of 1.1-1.2 amperes per square centimeter. Under these conditions magnesium concentration in a magnesium-zinc melt reached 80/83 percent at a current yield of magnesium above 90 percent. Average power consumption 15 kilowatt hour for 1 kilowatt magnesium.

